

APPLICATION OF ^{63}Ni , PHOTO- AND CORONA DISCHARGE IONIZATION FOR THE ANALYSIS OF CHEMICAL WARFARE AGENTS AND TOXIC WASTES

J. Stach, J. Adler, M. Brodacki and H.-R. Döring

BRUKER-Saxonia Analytik GmbH, Permoserstr. 15, 04318 Leipzig, F.R.G.

1. INTRODUCTION

Over the past decade, advances in instrumental design and refinements in the understanding of ion molecule reactions at atmospheric pressure enabled the application of Ion Mobility Spectrometry (IMS) as a simple inexpensive and sensitive analytical method for the detection of organic trace compounds [1-6]. Positive and negative gas-phase ions for ion mobility spectrometry have been produced by a variety of methods, including photo-ionization [7], laser multiphoton ionization [8], surface ionization [9], corona discharge ionization [10]. The most common ion source used in ion mobility spectrometry is a radioactive ^{63}Ni foil which is favoured due to simplicity, stability, convenience, and high selectivity. If reactant ions like $[(\text{H}_2\text{O})_n\text{H}]^+$ or $[(\text{H}_2\text{O})_n\text{O}_2]^-$ dominate in the reaction region, nearly all kinds of compounds with a given proton or electron affinity are ionized. However, the radioactivity of the ^{63}Ni foil is one disadvantage of this ion source that stimulates the development and application of other ionization techniques.

In this paper, we report analyses of old chemical warfare agents and toxic wastes using Bruker RAID ion mobility spectrometers. Due to the modular construction of the measuring cell, the spectrometers can be equipped with different ion sources. The combined use of ^{63}Ni , photo- and corona discharge ionization allows the identification of different classes of chemical compounds and yields in most cases comparable results.

2. EXPERIMENTAL

Spectra were recorded with BRUKER RAID ion mobility spectrometers equipped with ^{63}Ni , photo- and corona discharge ion sources. A scheme of the RAID-1 is shown in Fig. 1. Further details were given elsewhere [11,12].

Most of the samples were investigated with field and laboratory methods. Whereas in field analyses air above soil samples (from surface or drill holes) and contaminated parts of production buildings were measured, the head space technique was used in the lab.

GAS AND CURRENT FLOW DIAGRAM

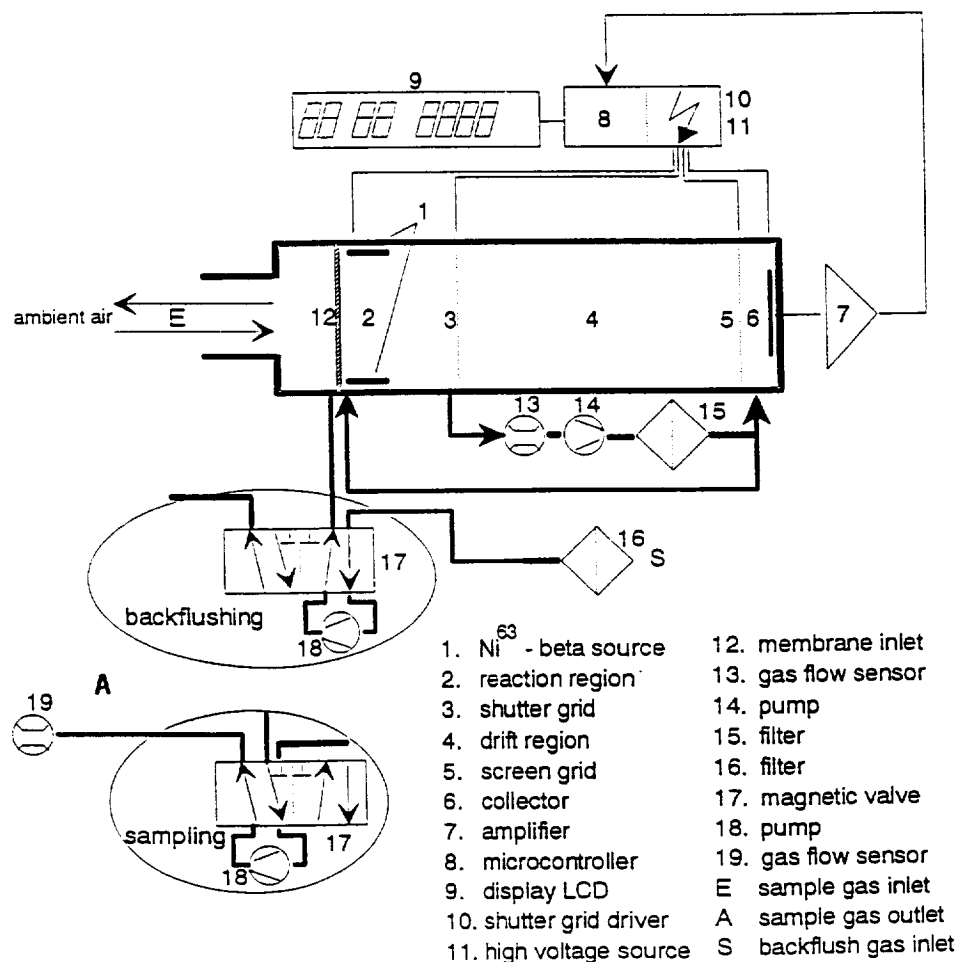


Fig.1: Gas and current flow diagram of the BRUKER RAID-1 IMS instrument

Head space analyses were carried out using 50 g of contaminated soil or 0.5 ml of liquids in glass flasks which were connected with the IMS by means of a Teflon tube. The samples were heated during 5 minutes from room temperature to 80°C. During the hole time, every 10 seconds, ion mobility spectra were recorded.

Results of the IMS investigations were confirmed by means of head space GC/MS (HP-5972) measurements using the following conditions: GC - column - DB-5, 30 m; carrier gas - helium; temperature program - 60°/2min. - 6°/min. - 280°C; injector temperature - 280°C; source temperature - 200°C; mass range - 40-400 amu; scan time - 1 sec.

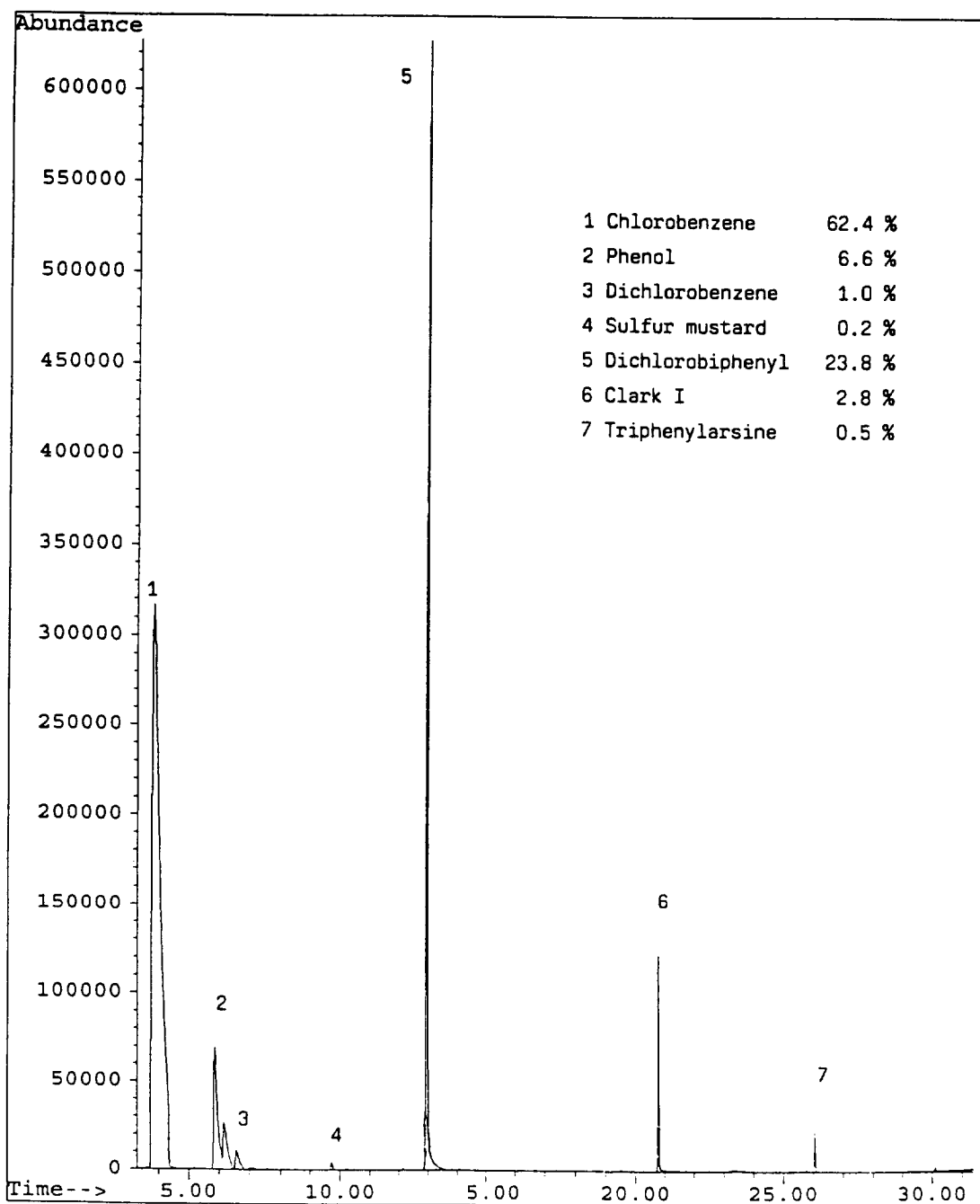


Fig. 2: Total ion chromatogram of the "Arsinöl" obtained by head space measurements

3. RESULTS

Usually old chemical warfare agents or residues resulting from production processes of warfare agents consist of a mixture of hazardous compounds. A typical example is that of sulfur or oxygen mustard which was used in mixtures with the German "Arsinöl" and other additives. The "Arsinöl" itself consists of 50 % phenyldichloroarsine, 35 % diphenylchloroarsine, 5 % triphenylarsine and 5 % trichloroarsine. Fig. 2 shows a total ion chromatogram obtained by head space GC/MS of a sample found on a production site for chemical warfare agents from the second world war. Main components of this sample are chlorobenzene, dichlorobenzene, phenol, chlorobiphenyl, chlorodiphenylarsine and triphenylarsine. Sulfur mustard is present in traces. The gas phase composition of the sample is given in the Fig 2.

The head space GC/MS investigations confirm the results of ion mobility spectrometry obtained with ^{63}Ni β -ionization in the negative ion mode. The corresponding spectrum (Fig. 3) shows typical signals with reduced ion mobilities $K_0 = 1.89, 1.51, 1.31$ and $1.17 \text{ cm}^2/\text{Vs}$. As indicated in Fig 3, these signals are mainly caused by chlorodiphenylarsine (Clark I) and triphenylarsine. Sulfur mustard could not be identified because its concentration (0.2 %) in presence of the arsenic containing compounds is too small.

^{63}Ni - β -IMS

ION MOBILITY SPECTRA OF NEGATIVE IONS

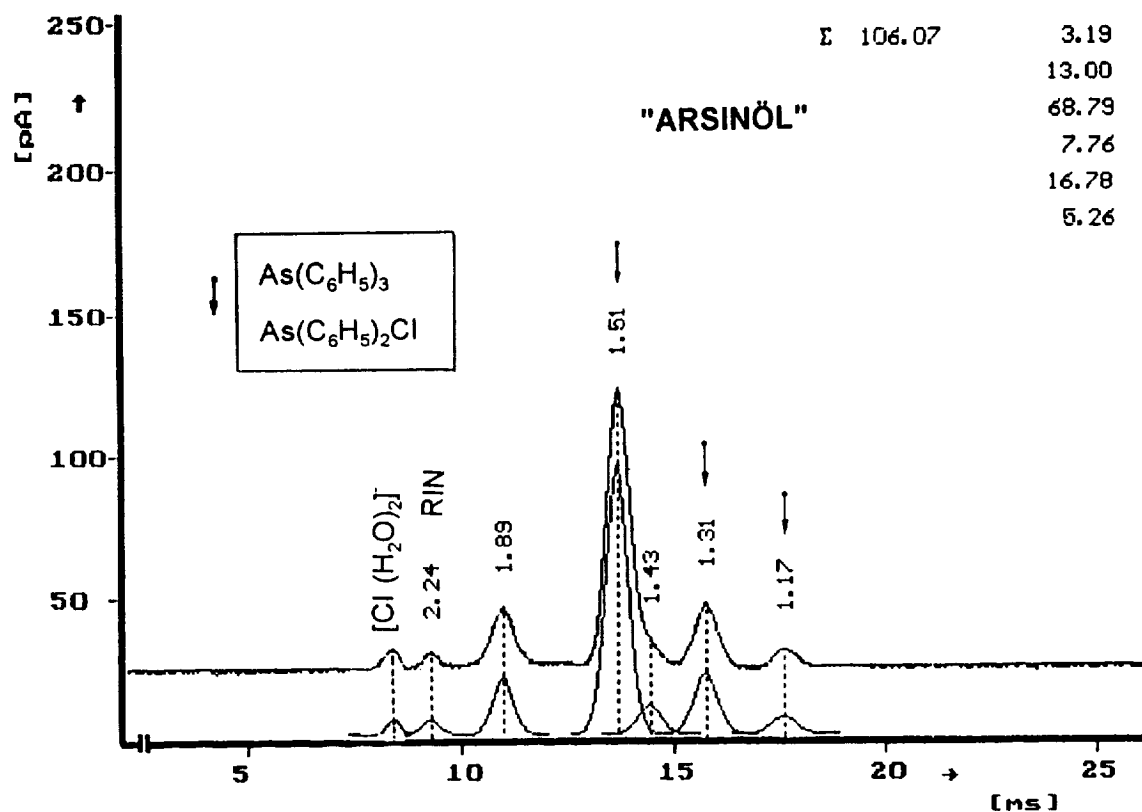


Fig. 3: Ion mobility spectrum (negative ions) of the "Arsinöl" obtained with ^{63}Ni β -ionization

The ion mobility spectrum recorded in the positive ion mode using a ^{63}Ni β -ion source shows a very complicated structure. However, using the information obtained from the negative ion mobility spectrum and the results of the GC/MS investigations, some peaks can be assigned to the arsenic containing compounds, chlorobenzene and the dichlorobiphenyl. The spectrum is shown in Fig. 4.

^{63}Ni - β -IMS ION MOBILITY SPECTRA OF POSITIVE IONS

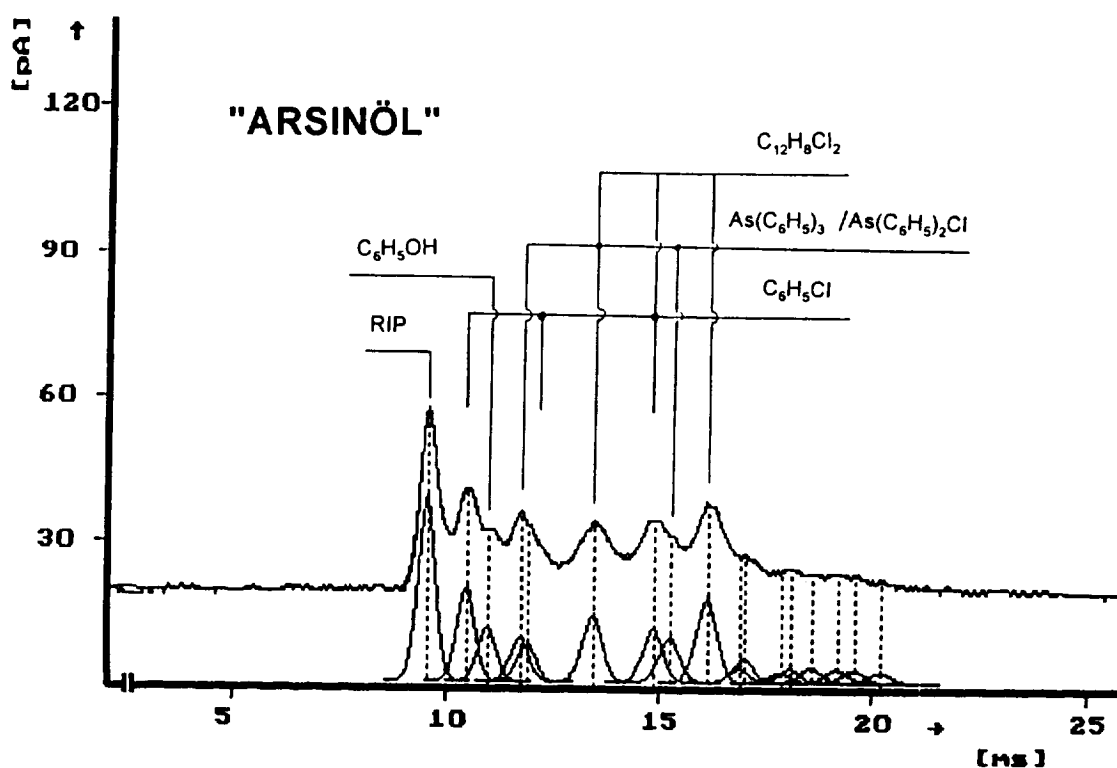


Fig. 4: Ion mobility spectrum (positive ions) of the "Arsinöl" recorded with a ^{63}Ni ion source

The GC/MS and IMS investigations suggest that this sample should be well suited for the application of photo-ionization because all components of the mixture are aromatic compounds. However, ion mobility spectra of the sample obtained in the positive ion mode by means of photo-ionization show very small signals. The intensity can be increased using a reagent gas[13]. The improvement in intensity is shown by means of a series of ion mobility spectra given in Fig. 5. Beside the signal caused by the reagent gas, peaks in the ion mobility spectra can be assigned to chlorobenzene, dichlorobiphenyl and the arsenic containing compounds.

UV-IMS ION MOBILITY SPECTRA OF POSITIVE IONS

"ARSINÖL"

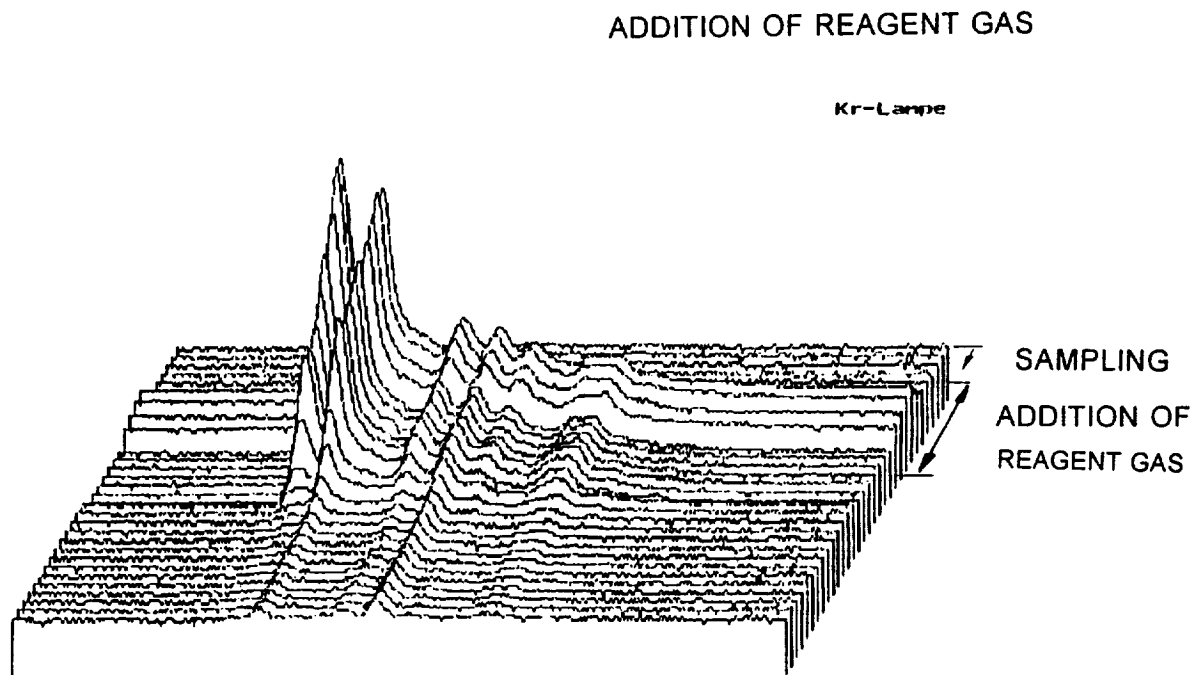


Fig. 5: Series of ion mobility spectra (positive ions) obtained by photo-ionisation and addition of reagent gas

Ion mobility spectra of negative ions recorded on spectrometers equipped with a photo-ionization source show reactant ions like CO_3^- , CO_4^- or $(\text{H}_2\text{O})_2\text{O}_2^-$ as known from ^{63}Ni ion sources. It is therefore not surprising that the spectra obtained for the "Arsinöl" are similar to those obtained by ^{63}Ni β -ionization. The spectrum is shown in Fig. 6. Peaks due to arsenic containing compounds are marked with arrows.

The corona discharge ion source which is still in process of development is considered as a substitute for the ^{63}Ni ion source. However, the formation of reactant and product ions depends on the applied field strength and geometrical arrangements of the electrodes. If both parameters are optimized, spectra as known from instruments with ^{63}Ni ion sources can be obtained. Fig. 7 shows a spectrum of positive ions recorded for the "Arsinöl". The shape of the measured spectrum comes close to that obtained with a ^{63}Ni ion source. The same is true for spectra recorded in the negative ion mode. However, in this case a pulsed corona discharge ion source has to be applied.

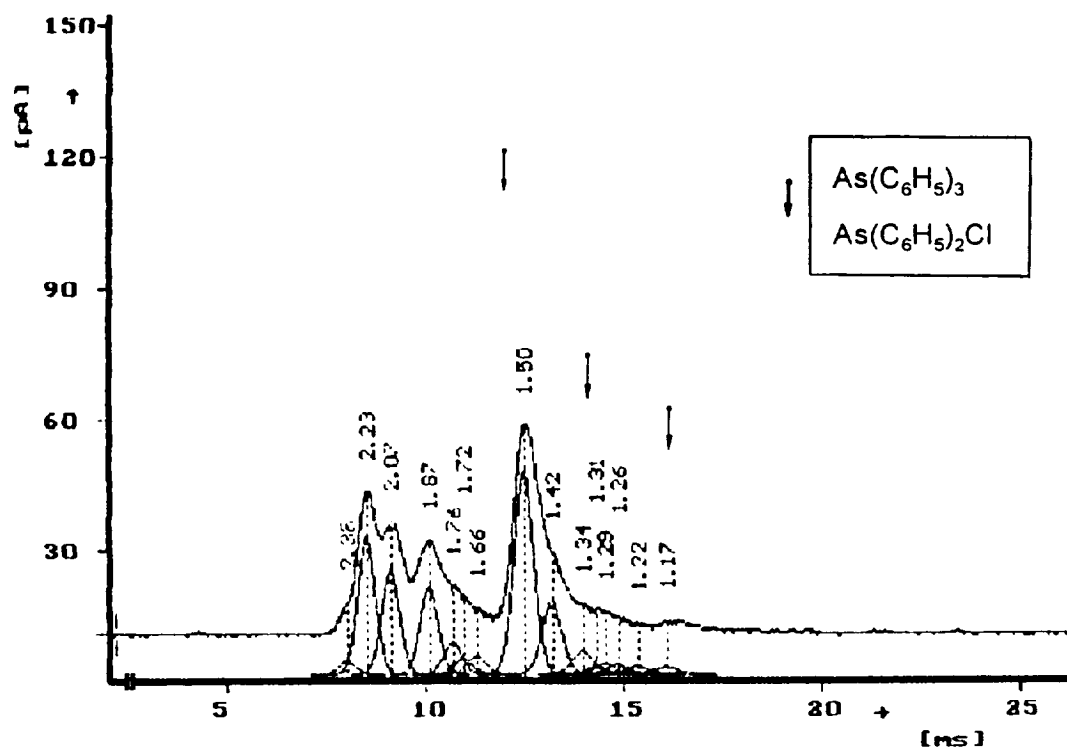


Fig. 6: Photo-ionization spectrum of negative ions of the "Arsinöl"

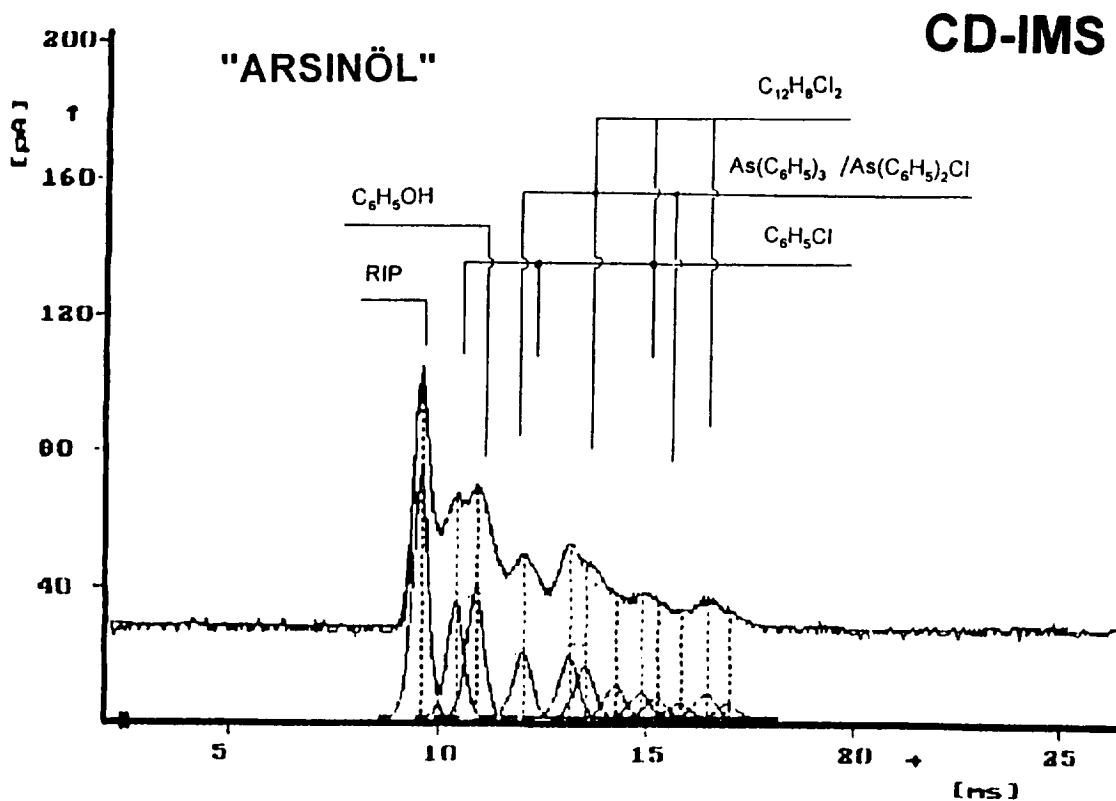


Fig. 7: Corona discharge ion mobility spectrum (positive ions) of the "Arsinöl"

4. DISCUSSION

A comparison of the results obtained with three ionization techniques shows that the investigated sample can be characterized in each case. As shown by the above described measurements, also in the case of old chemical warfare agents, which contain many additives or degradation products, the main components can be identified easily. However, up to now the ^{63}Ni ion source gives the best results for the detection of chemical warfare agents. The ionization processes are well known and the detection limits for compounds with given proton or electron affinity reach the lower ppb level. A disadvantage is the small linear range. From a practical point of view the high stability and life time of the ion source and the low power consumption of the instruments should be mentioned.

If photo-ionization is applied, reactant gases have to be used to get comparable results. Because of the formation of additional adduct ions, the spectra are not well resolved sometimes. The detection limits are found in the higher ppb or ppm level.

The sensitivity of the corona discharge ionization is comparable or better than that obtained with ^{63}Ni ion sources. The long time stability and the power consumption of the ion sources prevent a broad application in on-site analyses up to now.

4. LITERATURE

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